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# Liquid Phase Products and Solid Deposit Formation From Thermally Stressed Model Jet Fuels

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# LIQUID PHASE PRODUCTS AND SOLID DEPOSIT FORMATION FROM THERMALLY STRESSED

## MODEL JET FUELS

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### SUMMARY

The relationship between solid deposit and liquid degradation product formation was studied during the high-temperature (usually 400 °C) stressing of three hydrocarbon model fuels. A Jet Fuel Thermal Oxidation Tester was used to simulate high temperature and pressure engine fuel system conditions. Pure n-dodecane, ten percent tetralin in n-dodecane and pure 2-ethylnaphthalene were used as models of typical jet fuels and their individual components. The effects of fuel type, dissolved oxygen content, and reaction time were studied. Deposit formation on a heated cylindrical surface was measured by a light-reflectance technique and liquid products were assayed by capillary gas chromatography. All fuels were freshly purified before the stressing, but additional experiments were also performed using samples of 2-ethylnaphthalene which had been aged in contact with air for extended periods at 50 °C.

Experiments with n-dodecane showed that the deoxygenation only decreases deposit formation significantly when effective reaction time (contact with the hot surface) is kept short. The analytical results showed that mostly n-alkanes and corresponding 1-alkenes were formed as primary products. In the deoxygenated fuel, alkenes decreased at the long reaction time where deposit formation increased. This is consistent with the idea that more of these alkenes have participated in secondary reactions to form higher molecular weight deposit precursors. For the aerated fuel the amount of primary products remaining increased at the long reaction time. This indicated that the primary reaction rates were faster than the secondary precursor forming reactions which control the deposit formation.

When 10 percent tetralin was mixed with n-dodecane both the primary degradation of the dodecane and the formation of deposit was retarded slightly. The total amount of degradation products was higher than for n-dodecane alone, but the major products were from the broken saturated ring of tetralin which reacted preferentially to form alkylbenzenes. The latter compounds do not rapidly react to form deposit precursors.

The stressing of 2-ethylnaphthalene gave effects of reaction time and oxygen content different from those of n-dodecane. For the aerated, freshly distilled fuel increased time caused a large increase in deposit formation which was not found for the deoxygenated fuel. Deoxygenation was more effective in reducing deposit formation at the long reaction time. These effects are the opposite of the observations for n-dodecane. The primary decomposition products of 2-ethylnaphthalene were largely alkylbenzenes formed by complex splitting reactions of the aromatic rings. The deoxygenated fuel showed higher concentrations of these products remaining at the long reaction

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time than at the shorter reaction time, indicating a possible inhibition of the secondary soluble gum forming reactions by the primary products.

When 2-ethylnaphthalene was aged at 50 °C in contact with air, formation of several higher molecular weight products was observed. Subsequent stressing of these aged fuels formed no new products, only more of those already present. The measured amount of these products remaining after the stressing was changed very little either by variation of reaction time or by deoxygenation. But, the composition of the products did vary somewhat. The amount of deposit formation was changed very little by changing conditions of the stressing. There was no indication of self-inhibition of the gum-forming reactions for aged fuel, but there is an indication that the deposit may be soluble in the 2-ethylnaphthalene especially when the fuel is deoxygenated. An effect of aging alone on deposit formation was only observed for the long reaction time. The deposit level significantly increased due to the aging for both oxygen contents used. This effect was not found at the short reaction time.

Although the fuels used in this study are not practical jet fuels, they are typical components of real fuels. The general implications of our findings for real fuels are interesting. For both the paraffinic and naphthalenic fuels we have found that the longer exposure to a high temperature surface caused about the same amount of deposit formation regardless of the amount of dissolved oxygen in the fuel. Moreover, even for the shorter exposure time, deoxygenation does not significantly reduce deposit formation for the 2-ethylnaphthalene. This is especially true if the fuel has been aged at 50 °C for any significant length of time. Our work indicates that further study of the composition of the soluble gums is necessary to better understand the condensation reactions leading to solid formation both in the presence and absence of oxygen.

## INTRODUCTION

Research has been in progress for some time at the NASA Lewis Research Center to obtain an understanding of the mechanism of hydrocarbon fuel thermal instability (refs. 1 to 3). The final products of the degradation process are solid deposit and sediment which can cause serious problems in jet aircraft heat exchangers and engine fuel systems. Much previous work has shown the complexity of the hydrocarbon degradation problem (see, for example, refs. 4 to 7) and given useful information. However, we still do not have a complete understanding of the chemistry of the reactions involved. Previous work in this laboratory (refs. 1 and 2) has shown that the deposit forming tendency of a pure hydrocarbon depends on its structure, on the amount of oxygen dissolved in it and upon its previous history of heating. However, to understand the degradation chemistry involved, information must be obtained about the relationship between the primary liquid phase products and the amount of deposit formation. It is these liquid products which react further to form soluble gums which are considered to be the precursors of the solid formation (ref. 8). The identification and assessment of these products should help in the derivation of the mechanism of solid precursor formation during the decomposition of hydrocarbon fuels.

This report describes experiments in which two pure model hydrocarbons and one binary model fuel were thermally stressed and the primary products of

the reactions were identified and measured by capillary gas chromatography. These simpler fuels were used to make the interpretation of the analytical results simpler than it would be for a practical jet fuel. The apparatus and procedure described in reference 2 were used to stress the fuels and to measure the amount of deposit formed. For this investigation n-dodecane was used as the model for a typical alkane in a real fuel and 2-ethylnaphthalene was used as the model of an aromatic hydrocarbon. In addition a mixture of 10 percent tetralin in n-dodecane was also stressed. This mixture has been used by Daniel (ref. 9) as a simple model of actual Jet A turbine fuel in his study of storage and low temperature thermal stability. The binary mixture represents a hydrotreated fuel in which tetralin type compounds are formed by partial hydrogenation of naphthalenes. These three fuels were thermally stressed in a Jet Fuel Thermal Oxidation Tester (JFTOT) in the nominal temperature range of 250 to 400 °C. This temperature range was selected because of the lack of high-temperature thermal degradation data and because of the higher cycle temperatures of advanced-design gas turbine engines. Deposit formation on the cylindrical JFTOT tube was measured and liquid samples of the stressed fuels were analyzed by capillary gas chromatography using a flame ionization detector. The influence of dissolved-oxygen content was studied by testing the fuels either fully aerated or completely purged of oxygen. In addition the effect of reaction time (time in contact with the heated JFTOT tube surface) was studied by using two different flow rates through the JFTOT.

## EXPERIMENTAL

### Hydrocarbon Fuels

The following hydrocarbons were used in this study after the purification indicated:

(1) n-Dodecane - The 99 mole percent pure product from Phillips Petroleum Co. was treated with concentrated sulfuric acid to remove olefins and aromatics. After being thoroughly washed and dried it was vacuum distilled at 8 to 10 mm pressure and refrigerated until use.

(2) Tetralin (Tetrahydronaphthalene) - The purified grade product from Fisher Scientific Co. was vacuum distilled at 8 to 10 mm pressure within a few days of use and was refrigerated until being used.

(3) 2-Ethylnaphthalene - The 99 mole percent pure product from Aldrich Chemical Co. was purified by vacuum distillation (8 to 10 mm pressure) and refrigerated until being used. Experiments were also performed with three different samples of the distilled fuel which had been aged for 37, 50, and 60 days in contact with air in an incubator at a temperature of about 50 °C. The aging fuel was opened to the air and shaken once a day to maintain the oxygen supply above the liquid surface.

### Apparatus

A commercially available JFTOT from Alcor, Inc. was used to thermally stress each fuel by having it flow over the electrically heated surface of a

316-stainless steel tube shown on the right in figure 1. The average reaction temperature for any trial was measured by a thermocouple inside the cylindrical tube, placed to measure the maximum wall temperature along the test section. A typical test section temperature profile is given in reference 2.

During any experiment samples of the stressed fuels were withdrawn immediately downstream of the heated test section using the sampling valve shown in figure 1. All samples were refrigerated except when being used for gas chromatographic analysis. Any sediment formed in the fuel is trapped by the test filter also just downstream of the test section. The resulting filter blockage causes a pressure drop which is measured by the U-tube manometer. For all hydrocarbons tested in this study no pressure drop was ever measured. Therefore, from this point on we will discuss only formation of hard deposit on the cylindrical wall of the JFTOT tube test section. This deposit was measured with an Alcor Mark 9 tube deposit rater (TDR), which converts light reflectance measurements from the rotating tube to arbitrary readings. These measurements give an arbitrary measure of the deposit formation per unit length at any position along the 60 mm test section length.

### Procedure

Stressing and deposit measurement. - Each fuel was stressed in two ways to vary the reaction time, i.e. the average time in contact with the hot metal surface. The stressing time was either 40 min at a flow rate of 3 cm<sup>3</sup>/min or 120 min at a flow rate of 1 cm<sup>3</sup>/min. This procedure stressed the same volume of fuel at average reaction times of 12 and 36 sec respectively. A constant pressure of 3447 kPa (500 psig) was used for all trials and an average reaction temperature (as described above) of 400 °C was used for most experiments. Temperatures of 250 and 350 °C were used for a few trials.

An arbitrary measure of the deposit formation on any tube was obtained by plotting TDR reading versus tube position and measuring the area under the resulting curves. Under the assumption that each measurement is proportional to the deposit formation per unit length at a given position, the measured area gives a relative measure of total deposit amount on the tube. Previous work (refs. 1 and 2) showed that this is a reasonable assumption as long as the individual reading does not exceed 40.

Experiments were performed for two extremes of dissolved oxygen concentration in the fuel. Each sample was either aerated for 20 min or purged with nitrogen for about 30 min before being stressed. The aeration gave a saturated oxygen content of about 70 to 80 ppm and the nitrogen purge deoxygenation gave an oxygen concentration of approximately 2 to 3 ppm in the fuel.

Analytical procedure. - The thermally stressed fuel was analyzed by a capillary gas chromatograph equipped with a hydrogen flame ionization detector (FID) and split injector. The column was 60-m fused silica with the internal diameter of 0.25-mm coated with methyl silicone oil. Separation of degradation products was accomplished by programming the oven at 2°/min beginning at 50 up to 280 °C. The carrier gas was helium at a flow rate of 1-ml/min. With these analytical parameters nonpolar hydrocarbons are separated with good resolution for detecting the presence of individual alkane, alkene, and aromatic compounds. Another important advantage of using this analytical scheme

is the ability to detect some oxygenated compounds. For example, 2-octanone, 1-octanol, and 2, 6-dimethylphenol are detected with slightly better sensitivity than n-dodecane. Of course these compounds represent ketones, alcohols, and phenols, respectively.

For identification of detected compounds in the samples, retention times of the degradation products were matched against those from the standard compounds. n-Alkanes were assigned by matching the retention times of unknown gas chromatographic peaks with n-alkane standard peaks ranging from pentane (n-C<sub>5</sub>) to undecosane (n-C<sub>21</sub>). Other peaks were identified by matching the retention indices of the unknown peaks with the reference index values in which the retention behavior of a hydrocarbon is expressed in a uniform scale determined by a series of closely related standards (ref. 10). The retention indices (R.I.) were calculated using the following equation for linearly temperature-programmed capillary analysis.

$$R.I. = 100 \left( \frac{T_{\text{unknown}} - T_{n-C_z}}{T_{n-C_{z+1}} - T_{n-C_z}} \right) + 100 z$$

where

$T_{\text{unknown}}$  retention time of unknown

$T_{n-C_z}$  retention time of n-alkane standard immediately before the unknown

$T_{n-C_{z+1}}$  retention time of n-alkane standard immediately after the unknown

$z$  number of carbon atoms for the n-alkane standard immediately before the unknown

In matching the retention index values with the reference values, a deviation of less than 1.00 unit was allowed for the assignment of peaks. The identities of these gas chromatographic peaks are listed in table I, but further analysis by mass spectrometry would be warranted for confirmation of peak assignment. In addition to the retention indices, boiling points were estimated from the graph of boiling points of n-alkanes plotted against their retention times. Although the use of boiling points is not an accurate method of identification, it can improve the peak assignment based on the retention indices by providing further data toward the identification process.

In addition to the qualitative analysis, the amounts of the liquid phase degradation products were quantitated by integrating the peak areas of all components separated in the capillary column. Individual concentration was determined by the ratio of each component area to the total integrated area. The sum of the individual areas was obtained in table II to represent the amount of degradation products in the liquid phase.

## RESULTS AND DISCUSSION

### n-Dodecane

Figure 2 shows typical traces of TDR reading versus tube deposit position for aerated and deoxygenated n-dodecane stressed at 400 °C for the long

reaction time. The areas under these curves are one of the values listed for deposit formation in table III, which summarizes all results for stressing of pure n-dodecane. The table lists not only the deposit values but also the percentage of primary degradation products present in the stressed fuel, as measured by gas chromatography. The number for each experiment is the percentage of total integrated area on the chromatogram due to all detected products of the reactions.

Effects of deoxygenation. - Many previous investigations, including our own (ref. 1), have shown that reduced dissolved oxygen content in alkanes reduces the amount of deposit formation during thermal degradation. The results in table III for the short reaction time show that removal of oxygen reduces deposit formation by 41 percent while reducing the concentration of primary products remaining from 0.07 percent to 0.051, a 27 percent change. However, at the long reaction time deoxygenation caused only a 13 percent decrease in deposit formation, but reduces the primary product concentration from 0.099 percent of the stressed fuel to 0.047, a 53 percent decrease. These results show that the ratio of the deposit precursor formation rate to the oxidation rate increases with time in the absence of oxygen. The very large reduction in primary product concentration for deoxygenation at the long reaction time is probably caused by more of these products reacting to form deposit precursors.

Effect of reaction time. - The data in table III show that for aerated fuel, deposit amount increases only by 10 percent when reaction time is significantly increased. The amount of primary liquid products remaining also was increased from 0.070 to 0.099 percent. These results indicate that the formation of liquid products is faster and more extensive than the conversion of these products into deposit precursor molecules. When the fuel is deoxygenated, the increased reaction time results in a 62 percent increase in deposit formation with a slight decrease in the final primary product concentration from 0.051 to 0.047 percent of the stressed fuel. This again shows that, given extra reaction time, the deoxygenated primary products are efficiently converted into deposit precursors. The conclusion from all these results is that deoxygenation only reduces deposit formation significantly for n-dodecane if the reaction or contact time with the hot surface is kept short.

Analytical results. - The work of Mayo (ref. 8) has shown that the primary degradation products of different hydrocarbons have widely different abilities to react further to form deposit precursors. It is therefore, very important to determine the identities of primary degradation products of our stressed fuels and relate them to the observed deposit forming tendencies. Detailed analytical results for n-dodecane are summarized in figure 3 and table III.

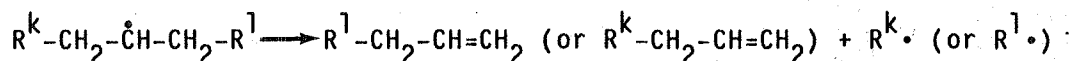
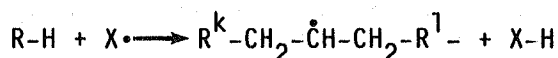
Deoxygenated, thermally stressed n-dodecane produced small amounts of n-alkanes ranging from pentane to undecane. The relative concentration of degradation products increased as the number of carbon atoms got smaller. In addition to n-alkanes, corresponding 1-alkenes were produced with the relative concentrations following the same trend as in the n-alkanes. Formation of n-alkanes ranging from methane to butane is probable, as discussed later, but these alkanes are in gaseous physical states and are not adequately analyzed by the methyl silicone coated capillary column used in this investigation. As shown in figure 3, the relative concentration of 1-pentene significantly changed as the average reaction time in the JFTOT tube was increased from 12

to 36 sec. As reaction time increased, the relative concentration of 1-pentene was reduced while all other degradation products increased in concentration. This indicated a significant contribution of 1-pentene through allyl radical reactions to either gum formation or deposit formation, since the latter also increased by 62 percent at the long reaction time.

In the deoxygenated dodecane an unknown compound with the estimated boiling point of 113 °C, which appears to be C<sub>8</sub> hydrocarbons, was present in large concentration. At the longer reaction time, the concentration of this compound slightly increased. When aerated n-dodecane was stressed, we found no evidence of this compound at either the short or long reaction times. By introducing oxygen into the n-dodecane, the yield of alkanes and alkenes was increased. Compared to the deoxygenated n-dodecane the ratio of 1-pentene to n-pentane was greatly reduced. Another interesting observation is the appearance of about 13 small concentration compounds at around the n-C<sub>22</sub> to n-C<sub>25</sub> region, corresponding to molecular weights of 310 to 352. These may be dimers and possibly trimers of small hydrocarbon molecules. Most likely they are polymers of alkenes formed by oxygenation since these higher molecular weight compounds were not produced in the absence of oxygen.

The ratio of alkane to alkene concentration for each carbon straightchain skeleton in the products can provide an insight into the mechanism of precursor formation. A semi-quantitative measurement of this ratio can be obtained from figure 3 for n-dodecane. For each carbon number from 5 to 11 the alkane and alkene peaks occur as a doublet, with the alkene to the left of the alkane. In table IV we have listed an approximate value of this ratio for several conditions at the 400 °C nominal stressing temperature. It can be seen from this table, first of all, that deoxygenation favors formation of alkenes at a constant reaction time. Also, for either the aerated or deoxygenated fuel, increasing the reaction time generally gave a higher ratio of alkanes to alkenes. These facts are consistent with the idea that alkenes are an important class of reactants which form the deposit precursors. The apparent consumption of alkenes at the long reaction time is accompanied by observed increase in deposit formation.

Degradation model. - In a degradation mechanism proposed by Hazlett (ref. 7) for n-dodecane, radical formation was followed by β-scission to yield 1-alkenes, and n-alkane formation by hydrogen transfer:

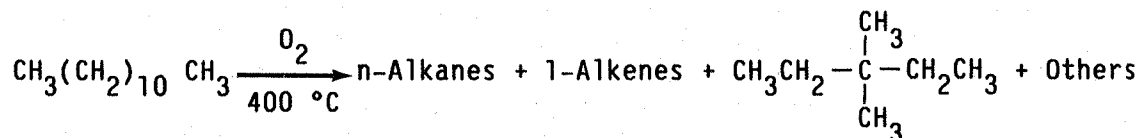
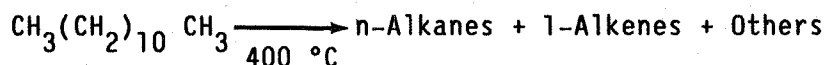


Subsequent radicals formed after the initial radicalization can further undergo β-scission or terminate by  $R\cdot + R\cdot \longrightarrow R-R$ .

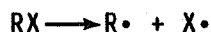
This decomposition was consistent with our observed formation of homologous series of n-alkanes and 1-alkenes in thermally stressed n-dodecane, although the presence of the unknown 113 °C (estimated) boiling point compound



and 3,3-dimethylpentane could not be explained by this model. For our system we can write



Also, this model could not predict the relative predominance of 1-pentene concentration. But, the initial radicalization step was consistent with the homolytic bond dissociation energies,  $D_{298}/\text{Kcal/mol}$ , in that the initial radical formation was at the secondary carbon atom (ref. 11). The bond dissociation energy is the heat of the reaction:



It is related to the strength of a chemical bond and heats of formation of free radicals by

$$D(\text{R-X}) = \Delta H_f^\circ(\text{R}\cdot) + \Delta H_f^\circ(\text{X}\cdot) - \Delta H_f^\circ(\text{RX})$$

$$D(\text{R-R}) = 2\Delta H_f^\circ(\text{R}\cdot) - \Delta H_f^\circ(\text{RR})$$

The relative ease of 1-alkene formation by  $\beta$ -scission was also evident from the bond dissociation energies which determine the molecular stability and thus the ease of free radical formation.

Intermolecular hydrogen transfer predominated over isomerization as shown by the lack of isomers in the profile of degradation products. Generally, alkyl radicals do not rearrange to form isomers, although the rearrangement of free radicals was reported to occur occasionally (ref. 12). The appearance of 3,3-dimethylpentane and the molecule with estimated boiling point of  $113^\circ\text{C}$  may be due to the rearrangement of free radicals.

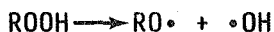
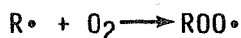
Once the chain propagation step is initiated the reaction proceeds at a fast rate to produce other radicals of smaller carbon number. These small radicals dimerize to form a longer chain by the termination step. However, deoxygenated n-dodecane did not show the presence of molecules with larger than 12 carbon atoms, although the flame ionization detector was only slightly less sensitive at higher carbon numbers. The aerated n-dodecane produced many molecules in the n-C<sub>22</sub> to n-C<sub>25</sub> range. Since aeration seemed to be the major factor in producing larger molecules, these molecules appeared to be oxygenated dimers (ref. 13) or polymers of alkenes induced by the aeration or oxygenation, as discussed later.

Decomposition of Hydroperoxide. - For aerated n-dodecane oxygen yields hydroperoxides which thermally decompose to form alkoxy and hydroxy radicals in which the unimolecular decay of the hydroperoxide is dependent on the

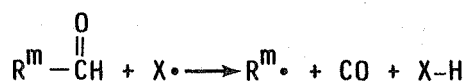
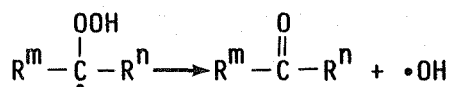
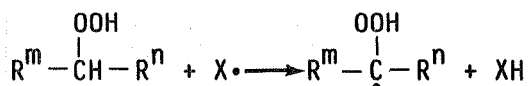
nature of the solvent (refs. 7 and 14). Oxygen reacts with a free radical to form a new radical:



This R-O-O $\cdot$  radical is less reactive than R $\cdot$  radical and thus breaks the chain and inhibits further growth of other radicals. The net effect is the slowing down of degradation reaction until all oxygen molecules have combined with free radicals. At the end of the inhibition period, the reaction resumes at its normal rate.



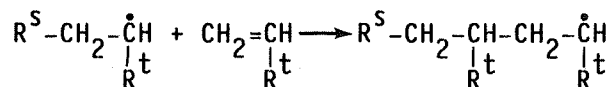
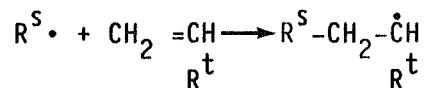
Some reactions of secondary ROOH and RO $\cdot$  species are as follows (ref. 7).



As in the pyrolytic degradation, free radical formation induced by oxygen would favor a secondary carbon atom in producing small carbon number molecules. Thus, subsequent thermal degradation of hydroperoxides would yield more alkyl radicals and alkanes. This increased yield was reflected by higher amounts of liquid products for aerated n-dodecane. The absence of carbonyl compounds may be due to the fast kinetic rate in converting alcohols and carbonyl compounds into soluble gum or solid deposit at the 400 °C temperature of this investigation.

Polymerization of alkenes. - Another important effect of aeration was the formation of many compounds around the n-C<sub>22</sub> to n-C<sub>25</sub> region. Since deoxygenated n-dodecane did not show these compounds, they most likely were the products of chain-reaction polymerization formed in the presence of oxygen(ref. 15). Polymerization was initiated by a peroxide radical which added to a molecule of alkene, and generated another free radical that

attached to another alkene molecule. Eventually the chain was terminated by the union of two radicals:

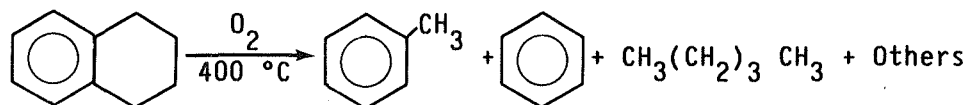


Termination is by the union of radicals.

#### Ten Percent Tetralin in n-Dodecane

Stressing experiments with this model fuel were performed at nominal temperatures of 250, 350, and 400 °C using the short reaction time of 12 sec. There is a sharp increase in deposit formation with temperature. The deposit and total product formation results are given table III for 400 °C. All mixtures were stressed fully aerated. The deposit results show that, for 400 °C, there is about 12 percent less formation of deposit than for pure n-dodecane at the same conditions.

The product formation shows that fewer peaks of n-alkanes and 1-alkenes were produced compared to aerated n-dodecane. But the total concentration of liquid phase degradation products at 400 °C increased from 0.070 percent for n-dodecane alone to 0.14 percent for tetralin in n-dodecane mixture. This increase in the concentration of degradation products was due to larger amounts of pentane, benzene, and methylbenzene among others.

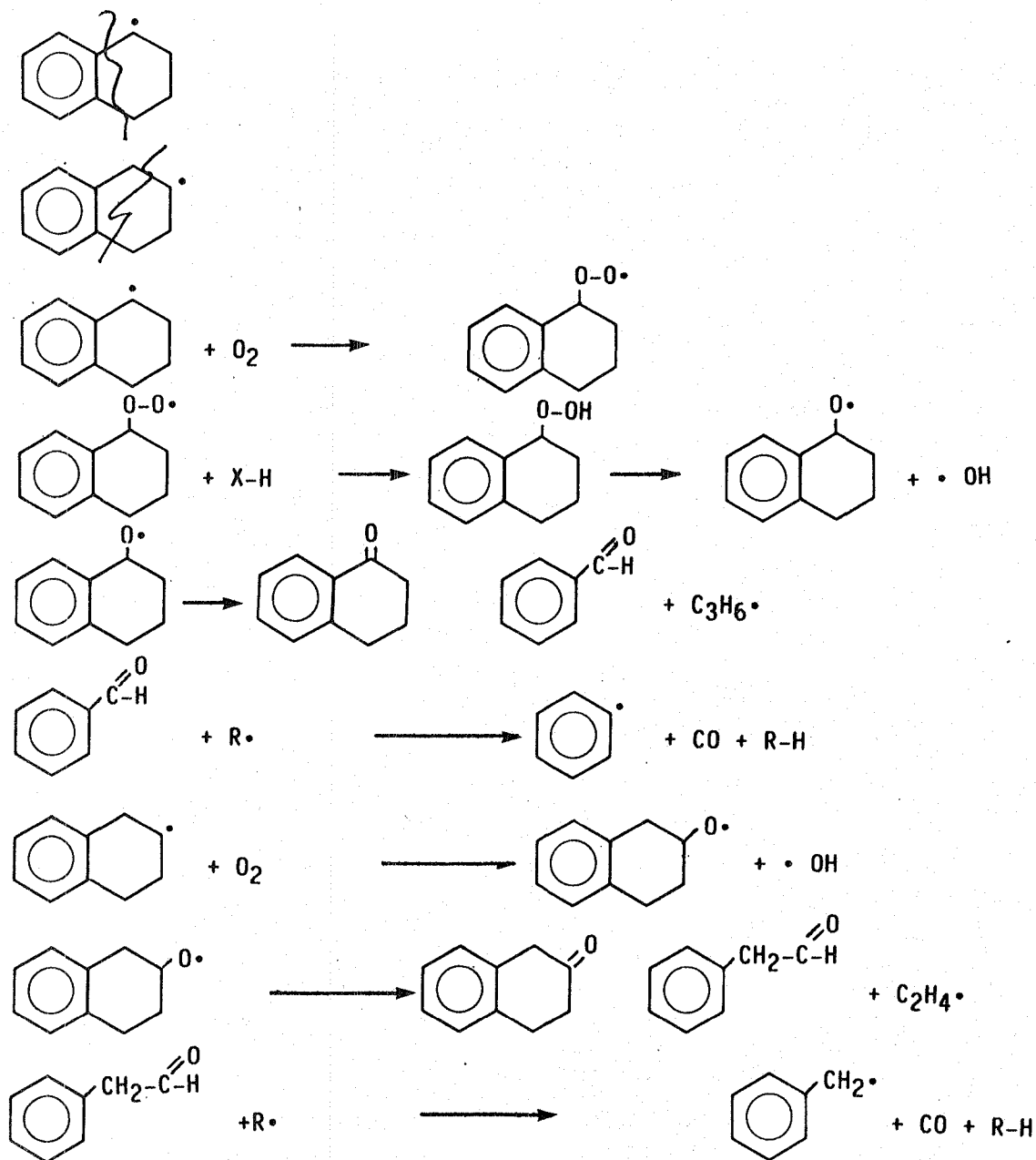


These molecules would have been the degradation products of tetralin in which the higher reactivity of tetralin allowed it to break down faster than n-dodecane. The net effect of 10 percent tetralin in n-dodecane was the retardation of decomposition rate of n-dodecane by highly reactive tetralin with corresponding decrease in deposit formation. The degradation products of tetralin did not rapidly react further to form deposit precursors.

A definite influence of temperature on the degradation process was observed as shown in figure 4. At 250 °C no liquid phase degradation product was detected at the analytical parameters used in this investigation. As temperature was raised to 350, 400, and 450 °C, the number of degradation products increased. Again, as the temperature increased, more tetralin was decomposed as compared to n-dodecane. At 350 °C, pentane, methylbenzene, and what appeared to be 1-pentene were produced. Both pentane and methylbenzene concentrations decreased slightly at 400 °C, but now a small amount of 109 °C boiling point molecules appeared. In one experiment at 450 °C, shown in figure 4, the 109 °C boiling point molecule completely disappeared while more

degradation products from n-dodecane were observed. Pentane and methylbenzene concentrations were larger, and still, the methylbenzene concentration was about twice larger than pentane.

The degradation of tetralin involved rupturing the saturated ring of the tetralin molecule. Benzene may have resulted from radical formation at the  $\alpha$ -position, and methylbenzene from radicalization at the  $\beta$ -position of the ring as follows.



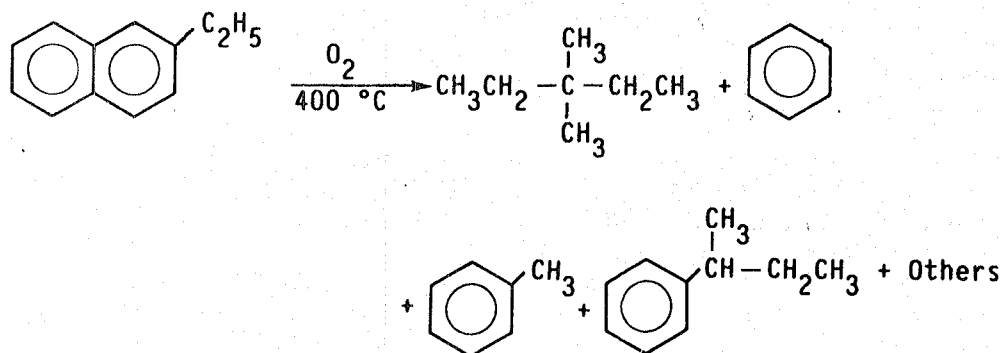
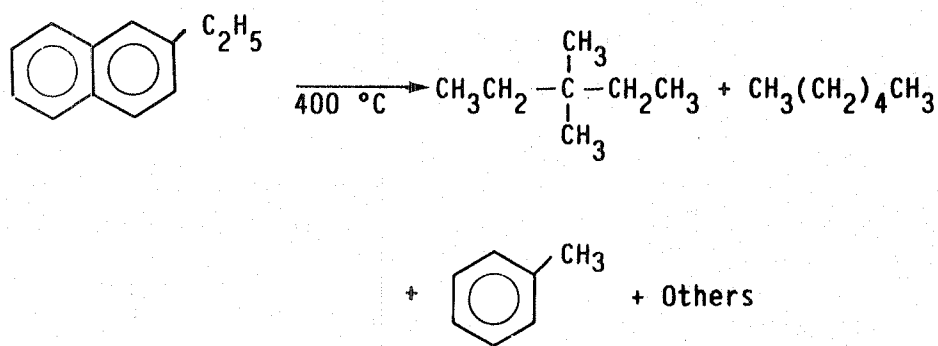
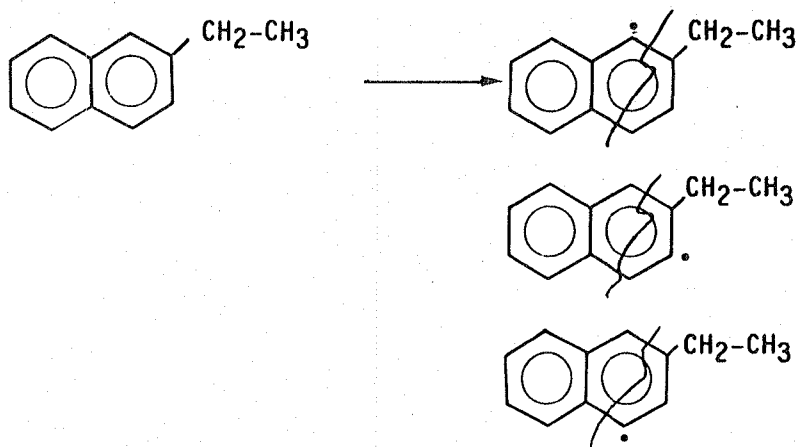
## 2-Ethyl-naphthalene

Four different samples of 2-ethyl-naphthalene were used in stressing experiments. All were vacuum distilled. One sample was stored at 4 °C under a blanket of nitrogen except when being used. We shall refer to it as freshly distilled fuel. The other three samples were aged for extended periods at 48 to 50 °C in contact with air. Aged fuel no. 1 had an aging period of 37 days, while aged fuel no. 2 was a mixture of two fuels with an average aging time of about 50 days. Aged fuel no. 3 was treated for a period of 60 days.

Experiments with freshly distilled fuel. - We observed that deposit formation for the freshly distilled fuel is almost doubled when the effective temperature is raised from 350 to 400 °C. Table V shows that, for 400 °C, the aerated fuel gives 40 percent more deposit formation when reaction time is increased from 12 to 36 seconds. However, when the fuel is deoxygenated, there is no change in deposit formation when reaction time is increased. These latter results are quite different from those with deoxygenated n-dodecane, where longer reaction time gave a very large increase in deposit formation. We can get a clue to the reason for this different behavior of 2-ethyl-naphthalene by looking at the final primary product concentrations in table V. For the deoxygenated fuel this product concentration increased significantly from 0.018 to 0.064 percent when reaction time was increased. This fact indicates that conversion of primary products to deposit precursors is fast at the short reaction time and slow at the long reaction time. This observation can be explained by the slow buildup of one or more primary products that inhibit the secondary reactions that form soluble gums and ultimately the solid deposits. The result is no significant change in deposit formation when reaction time is increased. On the other hand, with aerated 2-ethyl-naphthalene we notice a large decrease in final primary product concentration at the long reaction time, with a corresponding large increase in deposit formation. Apparently the primary oxidative degradation products are readily converted into deposit precursors. It should be mentioned that the results for two repeat samples of one experiment shown in table II show a problem with reproducibility. However, the qualitative trends are clear. The lack of quantitative reproducibility is due to the complexity and variability of the degradation reactions and also to the difficulty in detecting the minute amounts of products formed.

The effect of deoxygenation at a fixed reaction time is also different for 2-ethyl-naphthalene and n-dodecane. Table V shows that removal of dissolved oxygen from 2-ethyl-naphthalene decreases deposit formation by only 11 percent at the short reaction time and by 37 percent at the long reaction time. It has already been shown that the magnitude of the effect is approximately the reverse for n-dodecane at the two reaction times (table III). The effect of deoxygenation on final primary product concentrations (table V) is consistent with the idea that the precursor forming reactions are self-inhibited in the absence of oxygen at the long reaction time. Results show that deoxygenation reduces final primary product concentration from 0.075 to 0.018 percent at the short reaction time. However, at the long reaction time, deoxygenation increases the primary product concentration from 0.030 to 0.064 percent. Thus, at the long reaction time the deoxygenated primary products are not converted to gums and solid deposit as rapidly as the aerated primary products. This explains the 37 percent decrease in deposit formation due to deoxygenation at the long reaction time.

Decomposition products. - The liquid phase degradation products of 2-ethylnaphthalene were benzene, methylbenzene, sec-butylbenzene, and n-pentylbenzene among other compounds. Formation of these alkylbenzenes may have resulted from the radical formation at the naphthalene ring position and subsequent breakage of the molecule by rupturing the ring structure. Due to the complexity involved in the possible sites of radicalization and subsequent reactions, the degradation mechanism for 2-ethylnaphthalene could not be postulated at this time. Although the rupturing of the naphthalene ring was observed in this investigation, further support by theoretical treatment could not be considered since not enough literature values are available for the heats of formation of free radicals for substituted benzenes and naphthalenes. A partial mechanism is as follows:



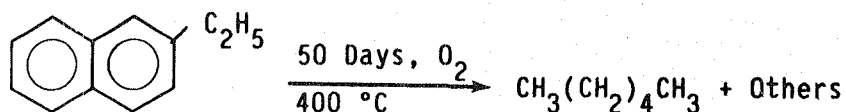
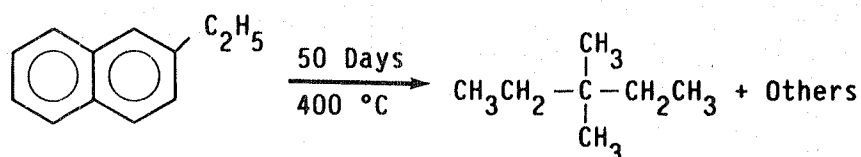
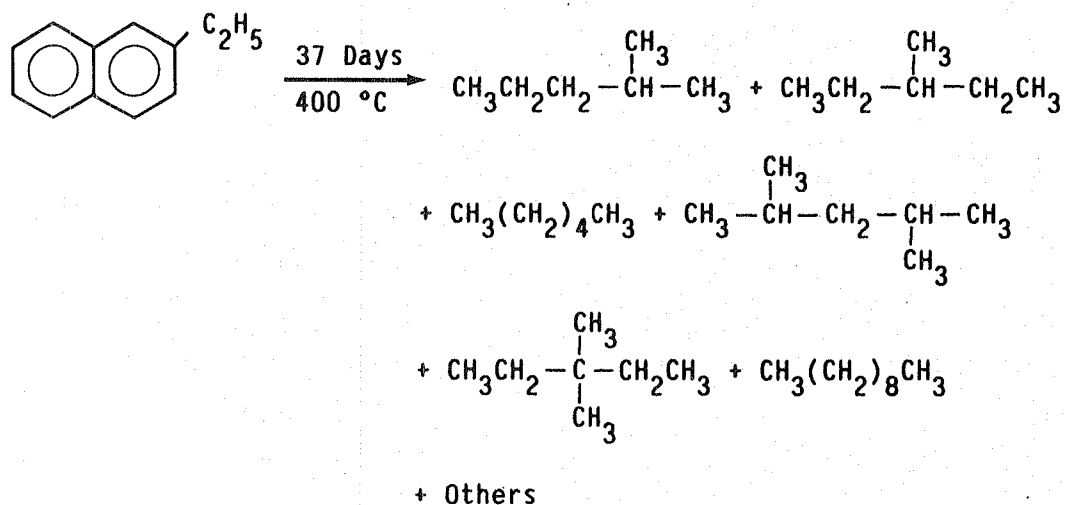
Experiments with aged 2-ethylnaphthalenes. - The three aged samples of 2-ethylnaphthalene were yellow colored, whereas the freshly distilled fuel was colorless. Gas chromatographic analysis of the aged but unstressed fuels showed the presence of several degradation products, especially around the n-C<sub>14</sub> to n-C<sub>17</sub> and n-C<sub>25</sub> to n-C<sub>27</sub> regions. This correspond to molecular weight ranges of 198 to 240 and 352 to 380. A check analysis of aged fuel no. 1 after 15 days of additional aging in a refrigerator showed a significant reduction in some of the degradation products. Other product concentrations stayed the same.

The effects of reaction time and deoxygenation are quite different for the aged fuels from those observed for the freshly distilled fuel. Aged fuel no. 1 was used, fully aerated, to determine the effect of reaction time. Table V shows that the deposit formation actually decreased by about 8 percent when reaction time was increased from 12 to 36 sec. The final concentration of primary products was only slightly greater for the longer reaction time. There is, therefore, no indication of self-inhibition of the deposit-precursor forming reactions in this case. It is possible that the deposit formed in these aged-fuel experiments is soluble in the 2-ethylnaphthalene. This physical effect may, at least partially, explain the decrease in deposit amount with increased reaction time.

The effect of deoxygenation was studied with aged fuel no. 2 at the long reaction time and aged fuel no. 3 at the short time. Table V shows that there is essentially no effect of deoxygenation on the amount of deposit formed and that the final concentration of primary products is decreased very slightly. This is not unexpected if one assumes that the aging process in contact with oxygen forms some reactive species which are the key participants in the precursor forming reactions. Analyses of the stressed fuels showed that all compounds formed in the aged but unstressed fuel were present, but in larger amounts. So stressing formed more of the same degradation products due to aging. No new ones were formed. The stressed-aged fuels turned red in color approximately 11 days after being stressed. A new analysis of these fuels showed that a few small-concentration compounds originally present had disappeared. Other compounds increased in concentration. Perhaps the red color was due to the absorption of ultraviolet radiation by condensed polynuclear aromatic compounds such as anthracenes, chrysenes, or phenanthrenes. Another significant effect of aging was the lack of alkylbenzenes in the stressed fuel degradation products. Instead of alkylbenzenes, alkanes, including isomers, along with large amounts of compounds in the n-C<sub>25</sub> to n-C<sub>27</sub> range were produced by stressing aged 2-ethylnaphthalene. With aged fuel no. 2, not as many substituted alkanes were produced by stressing at the long reaction time. Thus, aging conditions such as the temperature and the time influence the degradation reactions which are different from the unaged 2-ethylnaphthalene.

We have mentioned the small changes in primary product concentration for the aged fuels when either reaction time or oxygen content is changed. There are observed changes in the content of these products, however. With aged fuel no. 1, the longer reaction time produced larger amounts of hexane and substituted pentanes such as 2- and 3-methylpentanes and 2,4- and 3,3-dimethylpentanes. Concentrations of higher molecular weight compounds remained the same. With aged deoxygenated fuel no. 2, the stressed fuel products contained 3,3-dimethylpentane and relatively large amounts of high

molecular weight compounds. When this aerated fuel was stressed the 3,3-dimethylpentane disappeared and the concentrations of high molecular weight compounds were lower. In addition, small amounts of hexane and other compounds were formed. Some solid particles of brownish black color were also observed in the sample container. Although it is difficult to substantiate from this investigation, for aged 2-ethylnaphthalene the stressing may have encouraged the formation of solid particles that settled out of the liquid phase from the molecules in the n-C<sub>14</sub> to n-C<sub>17</sub> and n-C<sub>25</sub> to n-C<sub>27</sub> range which may be condensed or fused polynuclear aromatics. Some possible reactions are the following:





Finally we remark that a large effect of aging alone on deposit formation (at a fixed reaction time and dissolved oxygen content) was observed only at the long reaction time. The deposit formation was significantly increased for aged fuel no. 2 for both the aerated and deoxygenated fuels. The experiment with aerated, aged fuel no. 1 showed a decrease in deposit formation at the long reaction time. At the short reaction time there was a moderate increase of deposit for aged fuel no. 1, but no change for aged fuel no. 3 when all fuels were aerated. No comparisons were made for deoxygenated fuels.

#### CONCLUDING REMARKS

In this study we have determined the effect of several variables on the chemistry of hydrocarbon degradation and the formation of solid deposit on a high-temperature metal surface. Opposite effects of deoxygenation and changing reaction time were found for two different hydrocarbon types, an alkane and an alkylnaphthalene. For both types of hydrocarbon we found that a long exposure to the high temperature surface forms almost the same amount of deposit, regardless of the oxygen content of the fuel. Moreover, even at a short exposure time, deoxygenation does not significantly reduce deposit formation for the alkylnaphthalene, especially if it has been aged at about 50 °C for any significant length of time. Although different primary degradation products are formed in the presence and absence of oxygen, both types can react further to form soluble gums or solid-deposit precursors. Therefore our work indicates that further study of the composition of these secondary products is necessary to better understand the condensation reactions that lead to solid formation.

Although the hydrocarbons used in this study are not practical jet fuels, they are typical components of real fuels. Thus, the general implications of our results may have some application for real fuels. This is especially true for the effects of aging at the slightly elevated temperature of 50 °C. This treatment could simulate the long term storage of real fuels in hot, sunny climates. Further work is needed in identifying the primary and secondary products of the degradation process, especially any molecules that might act as inhibitors of the precursor-forming reactions.

#### SUMMARY OF RESULTS

Three model fuels, n-dodecane, 10 percent tetralin in n-dodecane and 2-ethylnaphthalene were thermally stressed in a Jet Fuel Thermal Oxidation Tester (JFTOT). Most of the experiments were done at an effective temperature of 400 °C. The relationship between solid deposit formation and the primary liquid phase products was studied by analyzing the stressed fuel as well as measuring the deposit formation. Capillary gas chromatography was used to identify the products of the reactions and investigate the mechanism of the decomposition. In addition to fuel type, the effect of varying reaction time and the amount of dissolved oxygen was studied. All fuels were purified just before the stressing. However, the 2-ethylnaphthalene was also stressed after it had been aged in contact with air for extended periods at 50 °C. The important results are as follows:

1. For n-dodecane the effect of deoxygenation in reducing deposit formation is much greater at short reaction time (12 sec) than at long reaction

time (36 sec). For aerated n-dodecane there is a relatively small increase in deposit when reaction time is tripled. However, when the fuel is deoxygenated, the same increase in reaction time causes a large increase in deposit formation. Thus, deoxygenation only reduces deposit formation for n-dodecane when reaction time is kept short.

2. The major primary degradation products in stressed n-dodecane are n-alkanes and the corresponding 1-alkenes. When aerated, the stressed fuel contained several compounds in small concentration in the C<sub>22</sub> to C<sub>25</sub> molecular weight region. These latter compounds were not present in the deoxygenated fuel and so probably resulted from alkene polymerization promoted by oxygen compounds. The amount of primary products decreased for the deoxygenated fuel when reaction time was increased. This fact is consistent with the observed increase in deposit formation since more of the primary products, especially alkenes, would have to condense together to form the deposit precursors. For aerated n-dodecane the amount of primary products increased at the long reaction time, indicating that the primary reaction rate of alkoxy and hydroxy radicals was faster than the secondary reactions which lead to deposit formation. The primary reactions involve radicalization at the secondary carbon atom followed by  $\beta$ -scission to yield n-alkanes and 1-alkenes with no apparent isomerization.

3. When ten percent tetralin was mixed with n-dodecane the degradation of n-dodecane and formation of deposit were retarded slightly. The total amount of degradation products was much higher than for n-dodecane alone, but the tetralin was preferentially decomposed to give alkyl benzenes which do not rapidly react to form deposit precursors. The degradation mechanism involved radicalization at the  $\alpha$ - and  $\beta$ -positions of the saturated tetralin ring and subsequent rupturing of the molecular structure.

4. When freshly distilled 2-ethylnaphthalene is stressed, the effects of reaction time and deoxygenation were somewhat different than for n-dodecane. When the fuel was aerated, the longer reaction time was significantly more effective in increasing deposit formation than it was for n-dodecane. However, when 2-ethylnaphthalene fuel was deoxygenated, the longer reaction time was much less effective than for dodecane in giving more deposit. Deoxygenation was more effective at the long reaction time in reducing deposit than at the short reaction time. Again this is opposite to the results for n-dodecane. The amount of degradation products remaining was decreased for 2-ethylnaphthalene by deoxygenation at the short reaction time but increased at the long reaction time. This fact, coupled with practically unchanged deposit formation at increased reaction time, indicates a possible inhibiting of the secondary gum forming reactions by the primary reaction products. The primary degradation reactions are very complex and involve the formation of alkyl benzenes and rupturing of the naphthalene ring.

5. When aged 2-ethylnaphthalene fuels were stressed, deposit formation was little changed by either increased reaction time or removal of the dissolved oxygen. The measured final concentration of primary products was about the same for all conditions, but the identity of the products was different for different conditions. In particular, the longer reaction time caused more hexane and substituted pentanes to be formed. For these aged fuels there was no indication of self-inhibition of the secondary gum-forming reactions. However, there is an indication that the deposit may be soluble in the ethylnaphthalene when the fuel is deoxygenated before stressing. Chemical analysis of

the aged, but unstressed, fuels showed the production of many higher molecular weight compounds in the C<sub>14</sub> to C<sub>17</sub> and C<sub>25</sub> to C<sub>27</sub> ranges. No new compounds were formed during stressing, but those formed by aging increased in concentration. For aged 2-ethylnaphthalenes, stressing did not form the alkylbenzenes that were observed for freshly distilled ethylnaphthalene. Instead, several alkanes, including isomers, were produced, along with large quantities of the C<sub>14</sub> to C<sub>17</sub> and C<sub>25</sub> to C<sub>27</sub> compounds.

6. For 2-ethylnaphthalene a large effect of the aging process alone on deposit formation was observed only for the long reaction time. The deposit formation was significantly changed due to this aging for both aerated and deoxygenated fuels. This effect was not observed for the short reaction time.

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TABLE I. - TENTATIVELY IDENTIFIED THERMAL DEGRADATION PRODUCTS  
IN THE LIQUID PHASE

(a) n-Dodecane

Butane, pentane, hexane, heptane, octane, nonane, decane, undecane, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 3,3-dimethylpentane; 113 °C b.p., C<sub>22</sub>-C<sub>25</sub> compounds.

(b) 10 percent Tetralin in n-Dodecane

Pentane, 1-pentene, benzene, methylbenzene, degradation products of dodecane; 109 °C b.p.

(c) 2-Ethyl-naphthalene

n-Pentylbenzene, benzene, methylbenzene, sec-butylbenzene, hexane, 3,3-dimethylpentane; 60, 85, 190, and 216 °C b.p., C<sub>27</sub> compounds.

(d) Aged 2-Ethyl-naphthalene

3,3-Dimethylpentane, 2-methylpentane, 3-methylpentane, hexane, 2,4-dimethylpentane, decane; C<sub>14</sub>-C<sub>17</sub> and C<sub>25</sub>-C<sub>27</sub> compounds.

TABLE II. - RELATIVE CONCENTRATIONS OF THE LIQUID PHASE  
DEGRADATION PRODUCTS

(a) n-Dodecane

Unstressed	0 percent
Deoxygenated, 3 cm <sup>3</sup> /min, 400 °C	0.051 percent
1 cm <sup>3</sup> /min, 400 °C	0.047 percent
Aerated, 3 cm <sup>3</sup> /min, 400 °C	0.070 percent
1 cm <sup>3</sup> /min, 400 °C	0.099 percent

(b) 10 percent Tetralin in n-Dodecane

Unstressed	0 percent
Aerated, 3 cm <sup>3</sup> /min, 250 °C	0 percent
350 °C	0.49 percent
400 °C	0.14 percent

(c) 2-Ethyl-naphthalene

Unstressed	0 percent
Deoxygenated, 3 cm <sup>3</sup> /min, 400 °C	0.018 percent
1 cm <sup>3</sup> /min, 400 °C	0.064 percent
Aerated, 3 cm <sup>3</sup> /min, 350 °C	0.065 percent
400 °C	0.13 percent
repeat	0.022 percent
1 cm <sup>3</sup> /min, 400 °C	0.010 percent
repeat	0.050 percent

(d) Aged 2-Ethyl-naphthalene

Unstressed, 23 days	0.23 percent
37 days (no. 1)	0.28 percent
50 days (no. 2)	0.21 percent
60 days (no. 3)	0.01 percent
Aerated, 3 cm <sup>3</sup> /min, 400 °C, 37 days (no. 1)	0.40 percent
1 cm <sup>3</sup> /min, 400 °C, 37 days (no. 1)	0.43 percent
400 °C, 50 days (no. 2)	0.35 percent
3 cm <sup>3</sup> /min, 400 °C, 60 days (no. 3)	0.19 percent
Deoxygenated, 1 cm <sup>3</sup> /min, 400 °C, 50 days (no. 2)	0.43 percent
3 cm <sup>3</sup> /min, 400 °C, 60 days (no. 3)	0.68 percent

TABLE III. - DEPOSIT FORMATION AND PERCENT PRIMARY PRODUCTS FOR  
n-DODECANE AND TETRALIN

[T = 400 °C.]

Fuel and condition	Reaction time = 12 sec		Reaction time = 36 sec	
	Deposit, arb. units	Percent product	Deposit, arb. units	Percent product
Pure n-dodecane; aerated	755	0.070	834	0.099
Pure n-dodecane; deoxygenated	446	0.051	723	0.047
10 percent tetralin + n-dodecane; aerated	651	0.14	---	-----

TABLE IV. - APPROXIMATE RATIO OF ALKANE TO ALKENE  
CONCENTRATION PRODUCED BY THERMALLY STRESSING  
n-DODECANE AT 400 °C

[Ratios less than 1.0 indicate higher alkene content than  
alkane.]

Carbon number	Reaction time = 12 sec		Reaction time = 36 sec	
	Deoxygenated	Aerated	Deoxygenated	Aerated
C <sub>5</sub>	0.2	1.5	0.6	1.2
C <sub>6</sub>	1.0	1.1	1.1	1.2
C <sub>7</sub>	1.0	1.1	0.8	1.2
C <sub>8</sub>	0.8	1.0	1.0	1.9
C <sub>9</sub>	1.0	1.5	1.0	1.1
C <sub>10</sub>	0.8	2.2	0.5	0.5
C <sub>11</sub>	---	0.5	(a)	2.0

<sup>a</sup>No alkenes and only trace amount of alkanes detected.

TABLE V. - DEPOSIT FORMATION AND PERCENT PRIMARY PRODUCTS  
FOR 2-ETHYLNAPHTHALENE

[T = 400 °C.]

Fuel and condition	Reaction time = 12 sec		Reaction time = 36 sec	
	Deposit, arb. units	Percent product	Deposit, arb. units	percent product
Fresh, aerated	765	0.075	1087	0.030
Fresh, deoxygenated	681	0.018	680	0.064
Aged no. 1, aerated	932	0.40	854	0.43
Aged no. 2, aerated	---	---	1220	0.40
Aged no. 2, deoxygenated	---	---	1200	0.35
Aged no. 3, aerated	759	0.19	----	-----
Aged no. 3, deoxygenated	706	0.68	----	-----



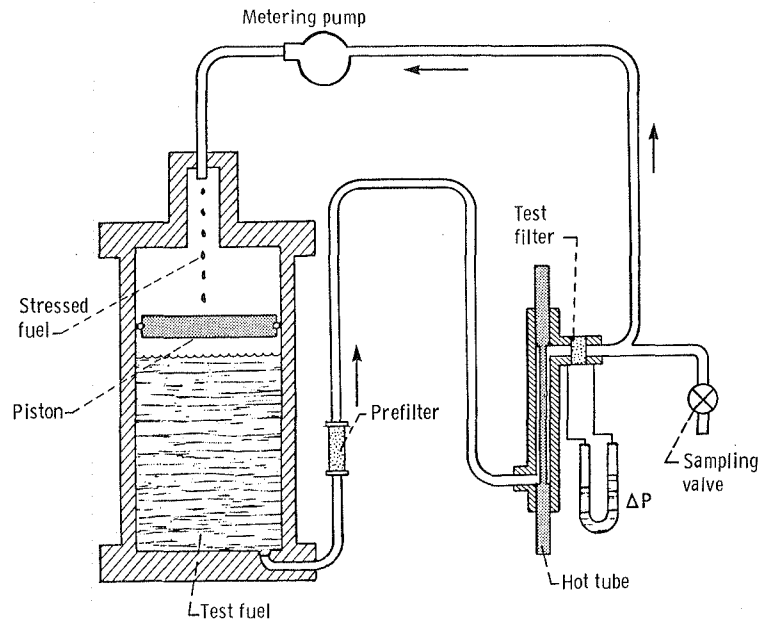


Figure 1. - Schematic of jet fuel thermal oxidation tester (JFTOT).

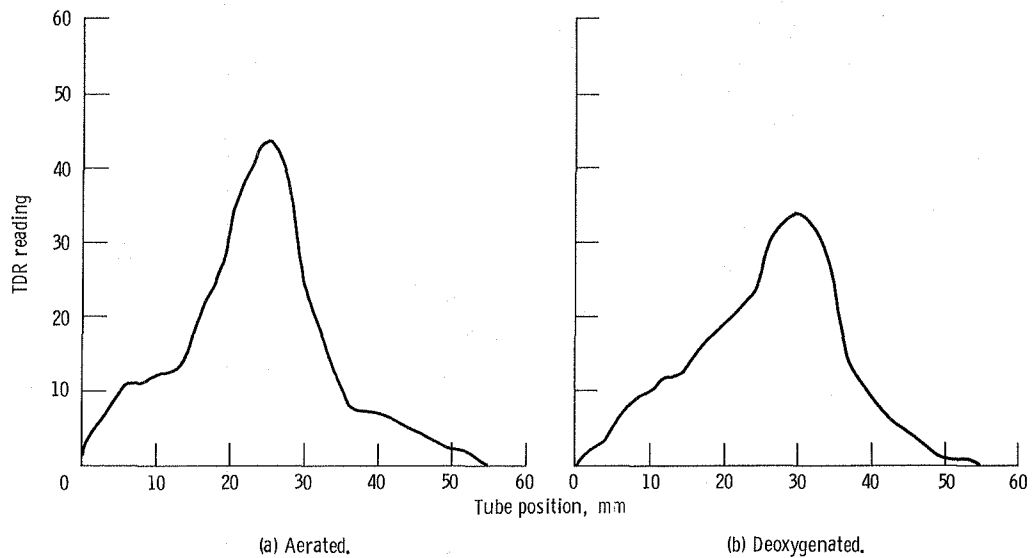


Figure 2. - JFTOT tube deposit measurement profiles for n-dodecane at a temperature of 400 °C and a reaction time of 36 sec.

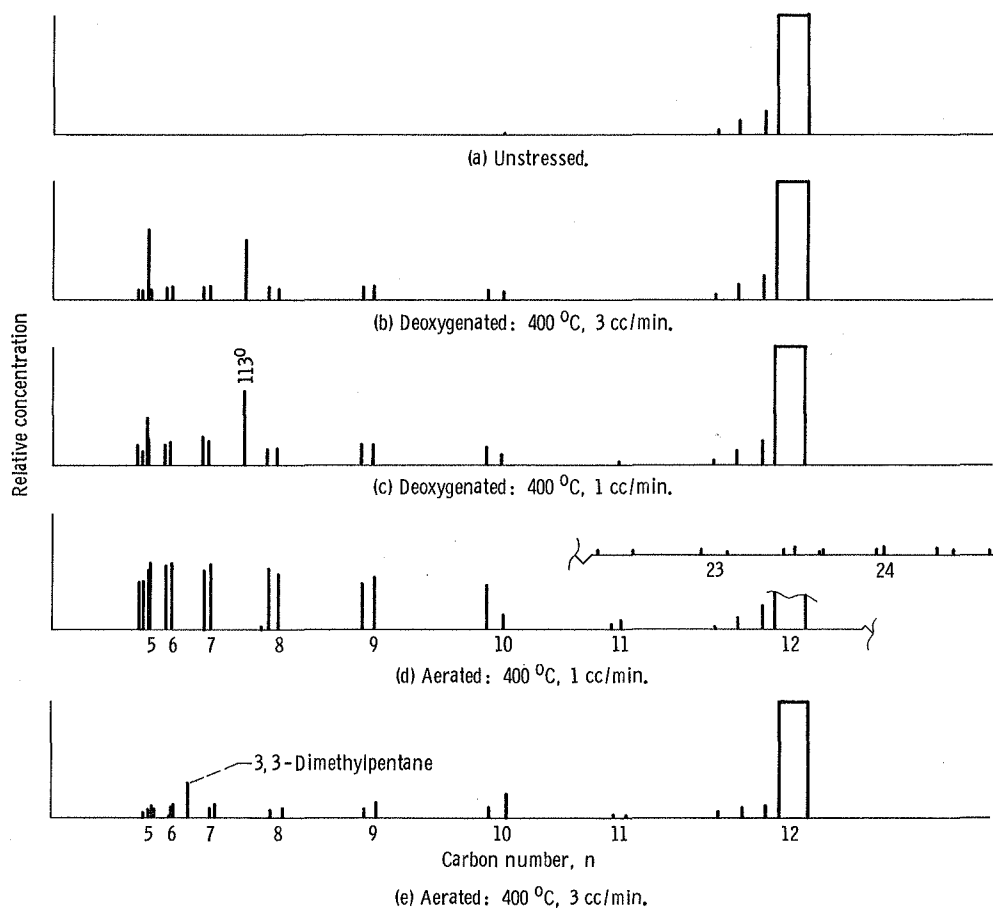


Figure 3. - Gas chromatograph profile of n-dodecane.

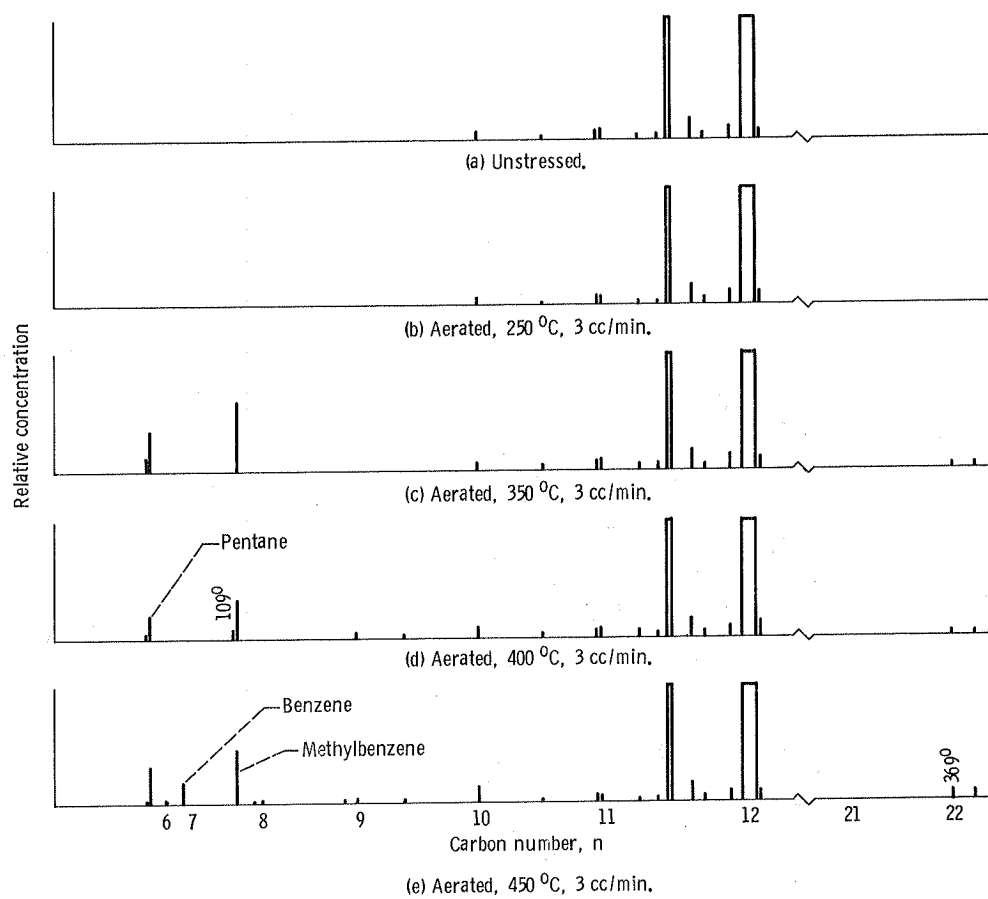


Figure 4. - Gas chromatograph profile of 10 percent tetralin in n-dodecane.

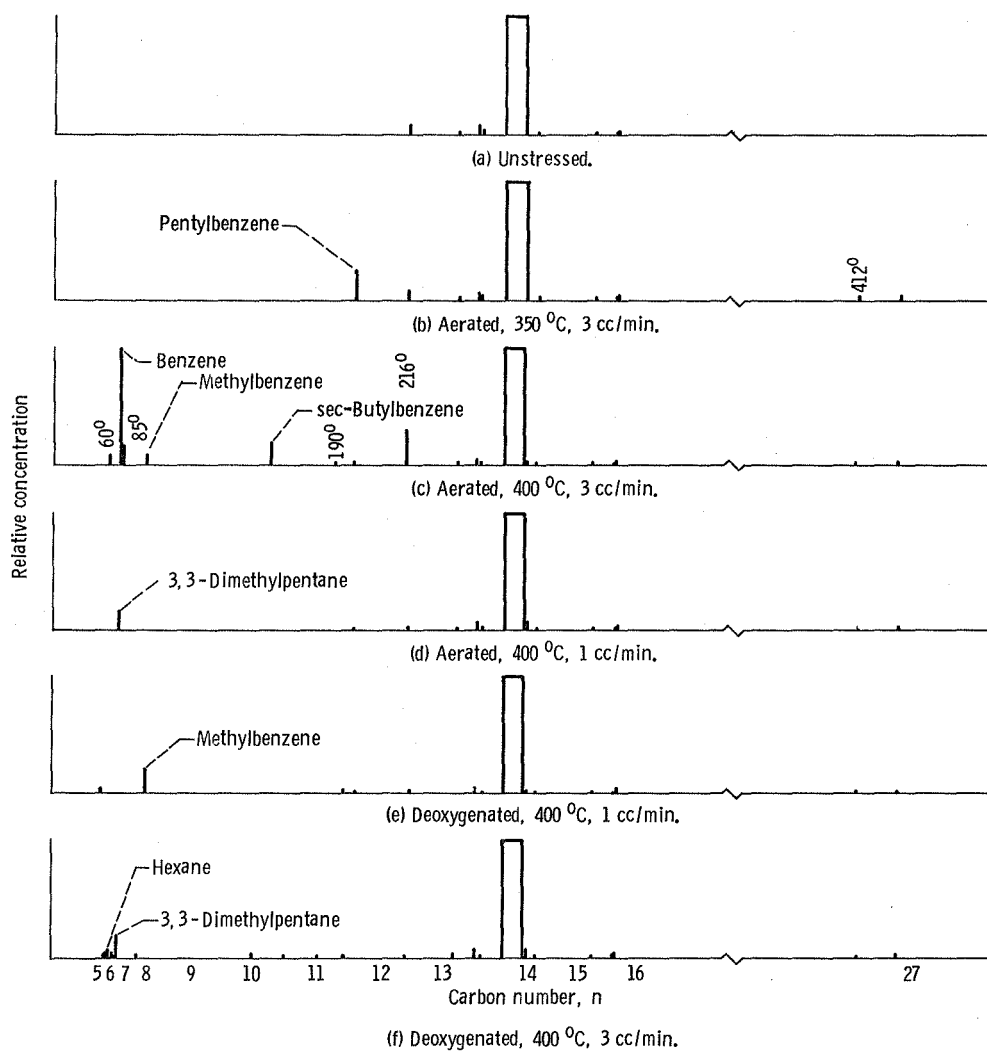


Figure 5. - Gas chromatograph profile of 2-ethylnaphthalene.

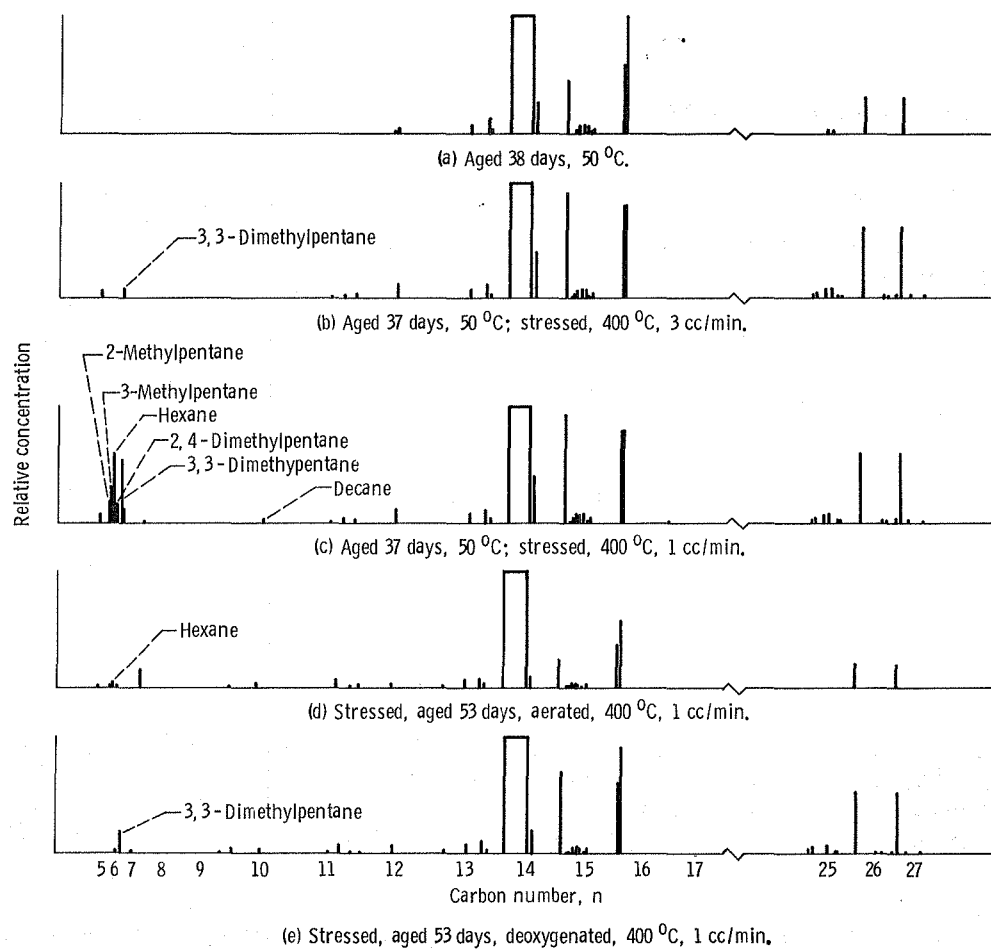


Figure 6. - Gas chromatograph profile of aged 2-ethylnaphthalene.

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16. Abstract  The relationship between solid deposit formation and liquid degradation product concentration was studied for the high temperature (400 °C) stressing of three hydrocarbon model fuels. A Jet Fuel Thermal Oxidation Tester was used to simulate actual engine fuel system conditions. The effects of fuel type, dissolved-oxygen concentration, and hot surface contact time (reaction time) were studied. Effects of reaction time and removal of dissolved oxygen on deposit formation were found to be different for n-dodecane and for 2-ethylnaphthalene. These two pure hydrocarbons are typical of the n-alkane and alkylnaphthalene components of practical jet fuels. When ten percent tetralin is added to n-dodecane to give a simpler model of an actual jet fuel, the tetralin inhibits both the deposit formation and the degradation of n-dodecane. For 2-ethylnaphthalene primary product analyses indicate a possible self-inhibition at long reaction times of the secondary reactions which form the deposit precursors. The mechanism of the primary breakdown of these fuels is suggested and the primary products which participate in these precursor-forming reactions are identified. Some implications of our results to the thermal degradation of real jet fuels are given.					
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